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Tunable Ionic-Conductivity of Collapsed Sandia Octahedral Molecular Sieves (SOMS)

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Abstract

This proposal focuses on the synthesis and characterization of "tunable" perovskite ceramics with resulting controlled strength and temperature of dielectric constants and/or with ionic conductivity. Traditional methods of synthesis involve high temperature oxide mixing and baking. We developed a new methodology of synthesis involving the (1) low temperature hydrothermal synthesis of metastable porous phases with "tuned" stoichiometry, and element types, and then (2) low temperature heat treatment to build exact stoichiometry perovksites, with the desired vacancy concentrations. This flexible pathway can lead to compositions and structures not attainable by conventional methods. During the course of this program, a series of Na-Nb perovskites were synthesized by calcining and collapsing microporous Sandia Octahedral Molecular Sieve (SOMS) phases. These materials were studied by various characterization techniques and conductivity measurements to better delineate stability and stoichiometry/bulk conductivity relationships. The conductivity can be altered by changing the concentration and type of the substituting framework cation(s) or by ion exchange of sodium. To date, the $Na_{0.9}Mg_{0.1}Nb_{0.8}Ti_{0.2}O_{3-\delta}$ shows the best conductivity.

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Introduction

Solid Oxide Fuel Cells (SOFCs) offer several advantages for the clean conversion of chemical energy into electricity including flexible fuel types (carbon-based), inexpensive non-noble metal catalysts, but most importantly, high efficiency. The enhanced efficiency of SOFCs is born out of its high operating temperature (1073 – 1273 K) allowing for high reaction rates and power densities.[1] However, technological difficulties arise at these operating temperatures: management of excess heat, the use of ceramic interconnects, thermal stresses and component failure. Lowering the operating temperatures can overcome these problems.[2] Yet, a major materials breakthrough is needed in order to maintain high ionic mobility at lower temperatures.

Development of new electrolyte materials is not a straightforward or simple issue. The new materials must possess ionic conductivities that are better than or similar to yttria-stabilized zirconia (3% YSZ, $\sigma = 0.17$ S/cm at 1273 K)[3] and be compatible with other fuel cell components. Perovskites, with nominal compositions of ABO_3, exhibit high ionic conductivities and are being studied for use as SOFC cathodes.[4] The ionic conductivity depends on the chemical composition and the extent of cation ordering. Traditional methods for synthesizing perovskites require high temperatures in order to form the desired phase. Hydrothermal synthesis at lower temperatures could increase the available composition space by allowing the formation of perovskites with metastable compositions or with higher defect concentrations.[5-10]

We have shown previously that heat treatment of metastable Sandia Octahedral Molecular Sieves (SOMS, $Na_4Nb_{4-2x}M_{2x}O_{12-x}\cdot H_2O$, where $0 \leq x \leq 0.4$ and M = Ti, Zr) phases at 450 °C yields pure perovskite phases ($NaNb_{1-2x}M_{2x}O_{3-x}$, where $0 \leq x \leq 0.1$ and M = Ti, Zr).[5] The SOMS phases convert directly to perovskites upon heating and the oxygen vacancy concentration depends upon the transition metal concentration. Perovskites formed from SOMS have lower exothermic heats of formation and are thought to exhibit more ionic disorder (desirable for ionic conductivity) compared to materials made by conventional methods.[7,11] (Similar results have been observed in condensed silicotitanates, where the ceramic phase "A" prepared hydrothermally is more stable than that prepared by solid-state methods.)[12] In addition, the SOMS compositions can be altered through framework substitution of the niobium, initially shown with Ti and Zr,[5] and more fully explored and reported herein. Further compositional change can occur through ion-exchange of the SOMS. Therefore, using the metastable SOMS as a reactant for the synthesis of the perovskites, it may be possible to synthesize compositions unobtainable through traditional methods. The perovskites prepared by this alternative low temperature route may show increased ionic conductivity due to composition, substitutional defects, and thermodynamic stability.

The research reported herein investigates the structure-property relationship between these hydrothermally mediated perovskites and their oxygen conductivities. The samples were synthesized from meta-stable SOMS precursors and their compositions were changed through framework substitution and/or ion-exchange. The perovskite structure was investigated by powder X-ray diffraction, thermogravimetric analysis, and chemical analysis. Ionic conductivities of the perovskites will be correlated to their structure and the stability of the original SOMS reactant. A full report is being published on this work.[13]

Experimental Section

Synthesis. Titanium (IV) isopropoxide, $Ti(OCH(CH_3)_2)_4$ (Aldrich, 99.999%), molybdenum (V) isopropoxide, $Mo(OCH(CH_3)_2)_5$ (Alfa Aesar, 99+%), germanium isopropoxide, $Ge(OCH(CH_3)_2)_4$ (Aldrich, 97%), zirconium isopropoxide isoproponol complex, $Zr(OCH(CH_3)_2)_4 \cdot (CH_3)_2CHOH$ (Aldrich, 99.99%), niobium (V) ethoxide, $Nb(OC_2H_5)_5$ (Alfa Aesar, 99%) and tellurium (IV) isopropoxide, $Te(OCH(CH_3)_2)_4$ (Alfa Aesar, 99.9%) were purchased and handled as received in an inert atmosphere, argon-filled box. Lithium nitrate, $LiNO_3$ (Aldrich, reagent plus), sodium hydroxide, NaOH (Alfa Aesar, 98%), magnesium chloride, $MgCl_2 \cdot 6H_2O$ (Aldrich, 99%), calcium chloride, $CaCl_2 \cdot 6H_2O$ (Aldrich, 98%), nickel(II) nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar, 98%), strontium chloride, $SrCl_2 \cdot 6H_2O$ (Aldrich, 99%), and yttrium chloride, $YCl_3 \cdot 6H_2O$ (99.9%). All reagents were used as received. All reactions were carried out in solutions of deionized water.

Detailed descriptions of model SOMS syntheses and conversions to perovskites are presented in the literature.[5] Substitution of the sodium atoms in $Na_4Nb_{3.2}Ti_{0.8}O_{2.9} \cdot H_2O$ was accomplished via ionic-exchange using metals salts. In a typical exchange reaction, 1 g of SOMS was added to 25 mL of an aqueous solution of metal salt (two equivalents of metal per sodium) and stirred for 1 h at room temperature. The sample was filtered and washed. The ion-exchange process was repeated two additional times. A more complete ion-exchange was achieved by refluxing the SOMS sample in 25 mL of an aqueous solution of metal salt (two equivalents of metal per sodium) overnight. Partial exchange was performed to maintain the orthorhombic perovskite structure, while complete exchange was done to study the affect of the A-site cation on the structure and conductivity.

Structural Characterization

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Siemens Kristalloflex D 500 diffractometer (Cu K_α radiation, Kevex detector, 40 kV, 30 mA; $2\theta = 5$ - 60 $^\circ$, 0.05° step size and 3 second count time) and used for crystalline phase identification. The phases were identified by comparison with the data reported in the JCPDS (Joint Committee of Powder Diffraction Standards) database. **Chemical compositions** were determined by ICP-MS spectroscopy at Galbraith Laboratories, Knoxville TN. **Differential thermal analysis (DTA) and thermogravimetric analysis (TGA)** of select samples were performed on a TA Instruments STD 2960 Simultaneous DTA-TGA with alumina crucibles and alumina powder reference. The heating profile consisted of a 5 °C min^{-1} linear ramp from ambient temperature to 750 °C in a static air atmosphere. **Ionic conductivities** were measured using a four-point conductivity probe. The powders were pressed into bars (nominally 2 mm x 2 mm x 20 mm) and heat-treated. Platinum wires were then attached at four spots with conductive silver-palladium paste to ensure good electrical conduction between the wires and the sample. The samples were then placed in a tube furnace and heated under a controlled temperature and atmosphere. A DC current source was connected to the two of the wires and the voltage drop across the other two wires was measure with a voltmeter. The conductivity was then calculated from the current, voltage and geometry of the sample. The samples were measure in air between 500 °C and 900 °C. Measurements were taken on 3% YSZ for comparison.

Results and Discussion

The hydrothermal synthesis described in the Experimental Section produced single phase samples with the microporous SOMS structure. Framework substitutions were made to study the affect of ionic radii, redox properties and the affect of stereo-chemically active lone pair of electrons. The phase purity of the framework substitutions is dependent upon the reaction time. With increasing reaction time, the inorganic subunits forming in solution are allowed to co-crystallize together into higher order structures. This is monitored by ex-situ X-ray diffraction (Figure 1) studies in which our reaction proceeds from solution to a 1-dimensional anionic cluster, the sodium hexaniobate ($Na_7(H_3O)(Nb_6O_{19})(H_2O)_{14}$), to the ordered 3-dimensional microporous SOMS and then to the condensed (collapsed) 3-dimensional orthorhombic perovskite structure ($NaNbO_3$) with space group Pbma. Exceptions are the Ge and Zr alkoxide mixtures, in which an intermediary layered 2-dimensional hexagonal illmenite phase ($NaNbO_3$, space group R-3) crystallizes in solution prior to the perovskite phase. In addition, the reaction time is dependent upon the amount of Ti-substitution; the reaction time increased with increasing Ti-substitution. These observations are consistent with previous studies.[5]

Single phase 20% Ti – SOMS was used for the substitution of various cations onto the sodium sites in the SOMS structure. In general, the room temperature ion exchange leads to partial replacement of the sodium ions and resulted in approximately 10 mole % exchange. However, repeating the process three times and under reflux at 90°C, leads to approximately 20 mole % exchange, a full exchange of the Na^+ ions.[5a]

The ionic conductivities of some of the perovskite samples are presented in Figure 3. The conductivities of the synthesized perovskites were measured and compared to the standard YSZ. The data indicates that the conductivity in air increases as transition metals are substituted into the framework structure (see comparison between $NaNbO_3$ end-member vs. 20% Ti-SOMS). The amount of metal substitution into the framework also affects the conductivity, indicating atomic scale variations affecting bulk properties. Furthermore, the conductivity decreases in the samples that were ion exchanged into 20% Ti-SOMS (heat treated to perovskites), except for the Mg^{2+} exchanged sample. The decrease in conductivity is unexpected as the exchange of mono-valent Na^+ for divalent cations (M^{2+}) might have resulted in cation defect sites in the perovskites. We speculate that charge compensation of the perovskite might be occurring through the incorporation of oxygen atoms; if additional oxygen atoms are incorporated into the structure, then the additional oxygen would occupy the space needed for the migration of the oxide anions and lead to a decrease in the conductivity. Another reason might be distortions in the perovskite structure resulting from differences in the atomic radii. These distortions would create a "tortured" path for the conduction of oxygen anions thereby, hinder the conduction of the oxygen anion.

The oxygen conductivity of $NaNbO_3$ (1.73×10^{-4} S/cm) is two orders of magnitude smaller than YSZ (1.73×10^{-2} S/cm) at 900 °C. The oxygen conductivity is affected by the substitution of Na atoms (A-site cation) by various metals. The $Na_{0.9}Mg_{0.1}Nb_{0.8}Ti_{0.2}O_{3-\delta}$ sample shows the highest conductivity (0.176 S/cm) at 900 °C; the conductivity is an order of magnitude higher than measured for 3% YSZ. It is important to note that the conductivities reported for the lithium exchanged sample are inaccurate; the sample was calcined at 1100 °C, thereby volatilizing the lithium atoms.

CONCLUSION

The SOMS structure is a low temperature alternative route for synthesizing perovskites for use as ionic conductors. The conductivity can be altered by changing the concentration and type of the substituting framework cation(s) or by ion exchange of sodium. To date, the $Na_{0.9}Mg_{0.1}Nb_{0.8}Ti_{0.2}O_{3-\delta}$ shows the best conductivity. Thermodynamic data is an indicator of SOMS framework stability and this stability correlates with the ionic-conductivity of the corresponding perovskite phase. The conductivity of the divalent substituted perovskites correlates linearly with the ionic radius of the divalent cation; a smaller ionic radius results in a higher conductivity.

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FIGURES

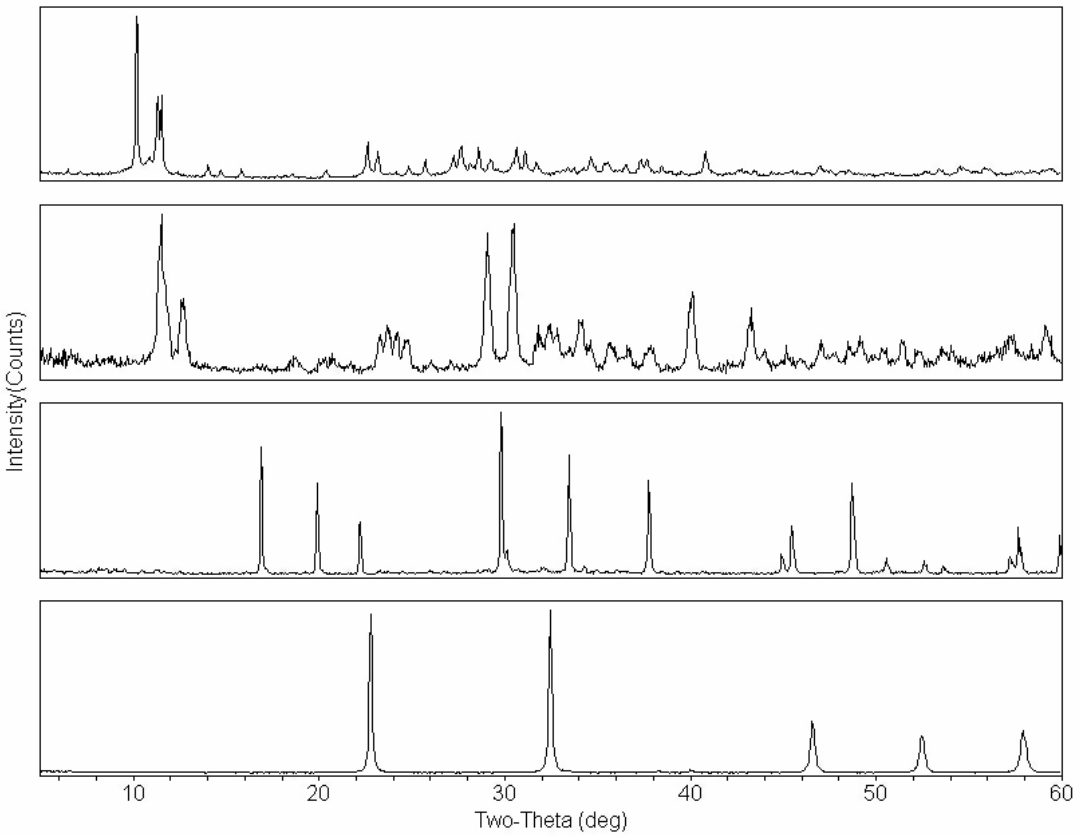

Figure 1. Ex-situ powder X-ray diffraction of phase transitions with time of SOMS to perovksite phases (follow top to bottom).

	6º phase	Hexaniobate	SOMS	Perovskite	69-2B phase
Na/Nb/Ti/O (20% Ti)	√	√	√	√	
Na/Nb/Ti/O (5% Ti)		√	√	√	
Na/Nb/Sn/O			√	√	
Na/Ta/Zr/O				√	
Na/Nb/Zr/O		√		√	√
Na/Nb/Mo/O		√		√	
Na/V/Ti/O		√		√	
Na/Nb/Hf/O				√	
Na/Ta/Ti/O				√	
Na/Sb/Ti/O				√	
Na/Nb/Ce/O				√	
Na/Nb/Ge/O			√	√	
Na/Nb/Te/O				√	

Figure 2. Table of samples synthesized as SOMS and SOMS-converted perovksites.

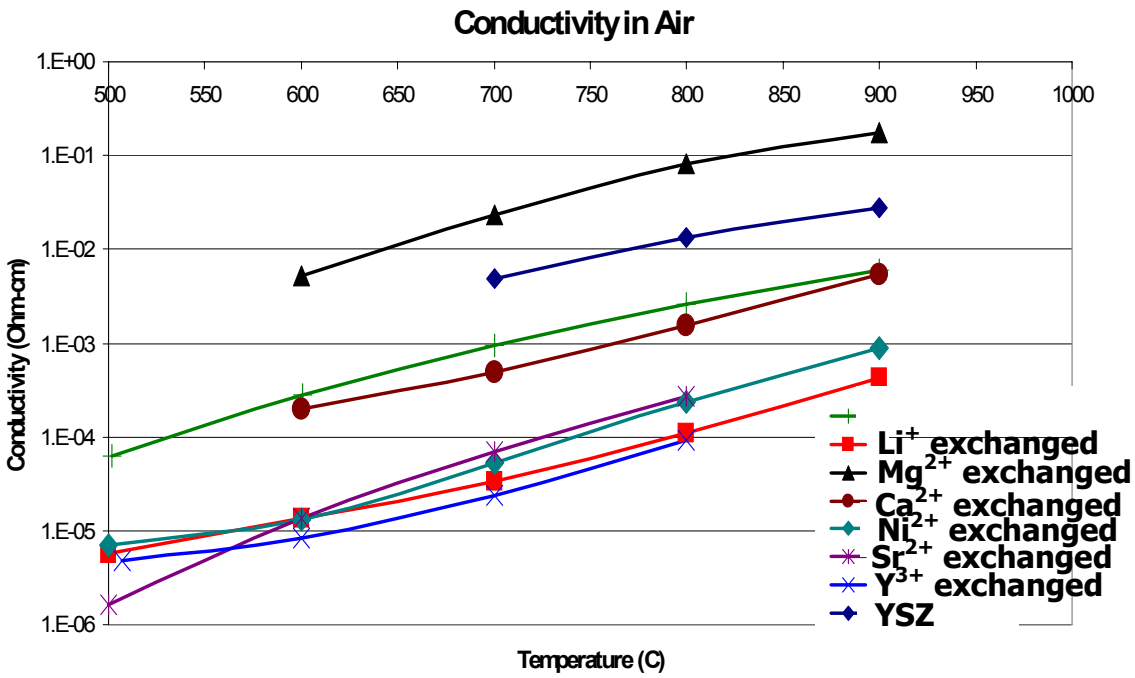

Figure 3. Conductivity vs. A-site substituted (through ion exchange of SOMS) perovksites.

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